

# Wet effluent parallel plate diffusion denuder coupled capillary ion chromatograph for the determination of atmospheric trace gases

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## Abstract

We describe an inexpensive, compact parallel plate diffusion denuder coupled capillary IC system for the determination of soluble ionogenic atmospheric trace gases. The active sampling area ( $0.6 \times 10$  cm) of the denuder is formed in a novel manner by thermally bonding silica gel particles to the surface of Plexiglas plates. The effluent liquid from the parallel plate diffusion denuder is collected and preconcentrated on a capillary preconcentrator column before analysis using a capillary ion chromatograph. Using  $\text{SO}_2$  as the test gas, collection efficiency is essentially quantitative at air sampling rates up to  $500 \text{ ml min}^{-1}$ . The system provides a limit of detection (LOD) of 1.6 parts per trillion for  $\text{SO}_2$  for a 10 min sampling period. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** Denuder; Effluent; Trace gases

## 1. Introduction

The determination of trace concentrations of atmospheric pollutant gases and aerosol particles has become increasingly important due to their adverse health effects. Diffusion based sampling systems are commonly used to separate gas phase analytes from concomitantly present aerosol particles, allowing the accurate determination of both species. The principles of diffusion based sampling systems have been reviewed [1,2].

Wet effluent diffusion denuders provide the desired characteristics of diffusion based sampling devices: a continuously renewed sampling surface and an easily changed scrubbing solution for sampling a variety of gases. With a diffusion denuder of closely spaced parallel plate construction, high gas collection efficiencies are also achieved with a minimum of particle loss [3]. Wet effluent denuders utilize an easily wettable sampling surface to continuously introduce a collection liquid that flows down the active surfaces of the denuder. Soluble gases of interest present in the sampled air stream diffuse to the walls and are absorbed by the flowing liquid. The liquid containing the collected analyte is then aspirated from the base of

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the denuder and analyzed using continuous or semi-continuous liquid phase analyzers. The diffusion coefficient of even the smallest aerosol particles is much smaller than that of a gas molecule and the aerosol is therefore efficiently transmitted through the denuder. If desired, the aerosol can then be collected and analyzed, free from the interference of gases. Wet effluent diffusion denuders (WEDDs) thus provide a simple, versatile, and easily automated air sampling strategy for a number of trace atmospheric gases that can be collected into a liquid scrubber.

We have previously demonstrated the near real time analysis of atmospheric trace level gases with a variety of wet effluent denuder designs [3–6]. The most efficient of these designs was based on a parallel plate geometry [3]. The design used two glass plates (50 × 300 mm active area) in which a central channel is formed by placing a 3 mm thick spacer between the edges of the plates. A silica-rich soft glass layer was formed on the surface of the glass plates to form a highly wettable soluble gas scrubbing surface. Aqueous hydrogen peroxide was pumped down the wettable plates to collect soluble gases of interest. Using this parallel plate design, quantitative gas collection efficiency was possible with air sampling rates up to 10 l min<sup>-1</sup>. Coupled to a standard ion chromatograph (IC), limits of detection in the sub parts per trillion (ppt) concentration range were observed for SO<sub>2</sub>, HONO, and HNO<sub>3</sub> using an 8 min sample time. Further, low particle losses enabled the accurate determination of aerosols following gas collection with the parallel plate WEDD [7,8].

For the simultaneous determination of several gases, it is convenient to separate the corresponding liquid phase analytes chromatographically before detection. Gases that form characteristic ions in solution can be easily determined by coupling the WEDD to an ion chromatograph (IC). Detector response in IC is related to the analyte concentration, similar to many other liquid phase separation systems that rely on flow through detectors. Typically, the aqueous analytes in the denuder effluent are therefore preconcentrated prior to separation and subsequent detection. Furthermore, air sampling flow rates are maintained as high as possible (while preferably main-

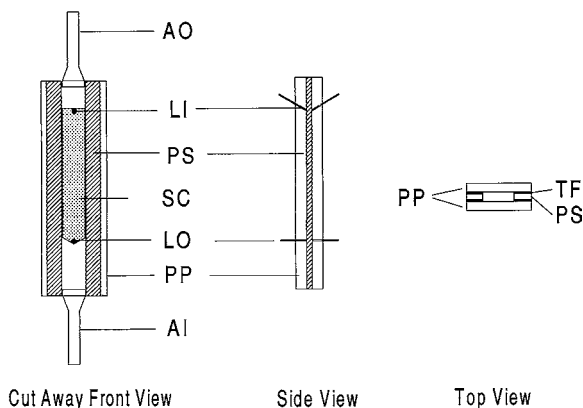


Fig. 1. Design of the parallel plate diffusion denuder. AI, air inlet; PP, Plexiglas plate; LO, liquid outlet; SC, silica coating; PS, Plexiglas spacer; LI, liquid inlet; AO, air outlet; TF, Teflon film.

taining quantitative collection efficiency) to increase the analyte concentration in the WEDD effluent. If WEDDs can be coupled to analytical systems with improved mass sensitivities, several potential advantages can accrue: miniaturization of the WEDD would be possible where liquid and air flow rates will both be lower relative to the larger scale devices, without a decrease in the analyte concentration in the effluent. Lower liquid flow rates would result in lower reagent consumption and hence, longer unattended operation

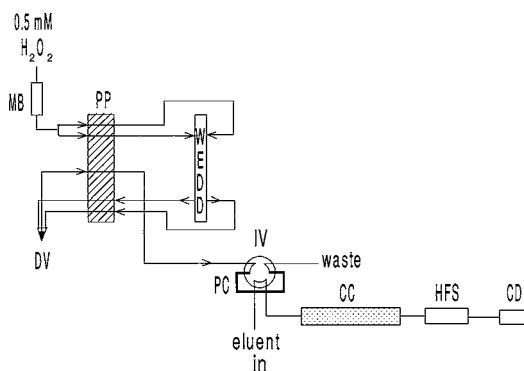


Fig. 2. Schematic of the liquid phase analytical system. MB, mixed bed ion exchange column; PP, peristaltic pump; WEDD, parallel plate wet effluent diffusion denuder; DV, degassing vial; IV, six port injection valve; PC, capillary preconcentrator column; CC, separation column; HFS, hollow fiber chemical suppressor; CD, conductivity detector.



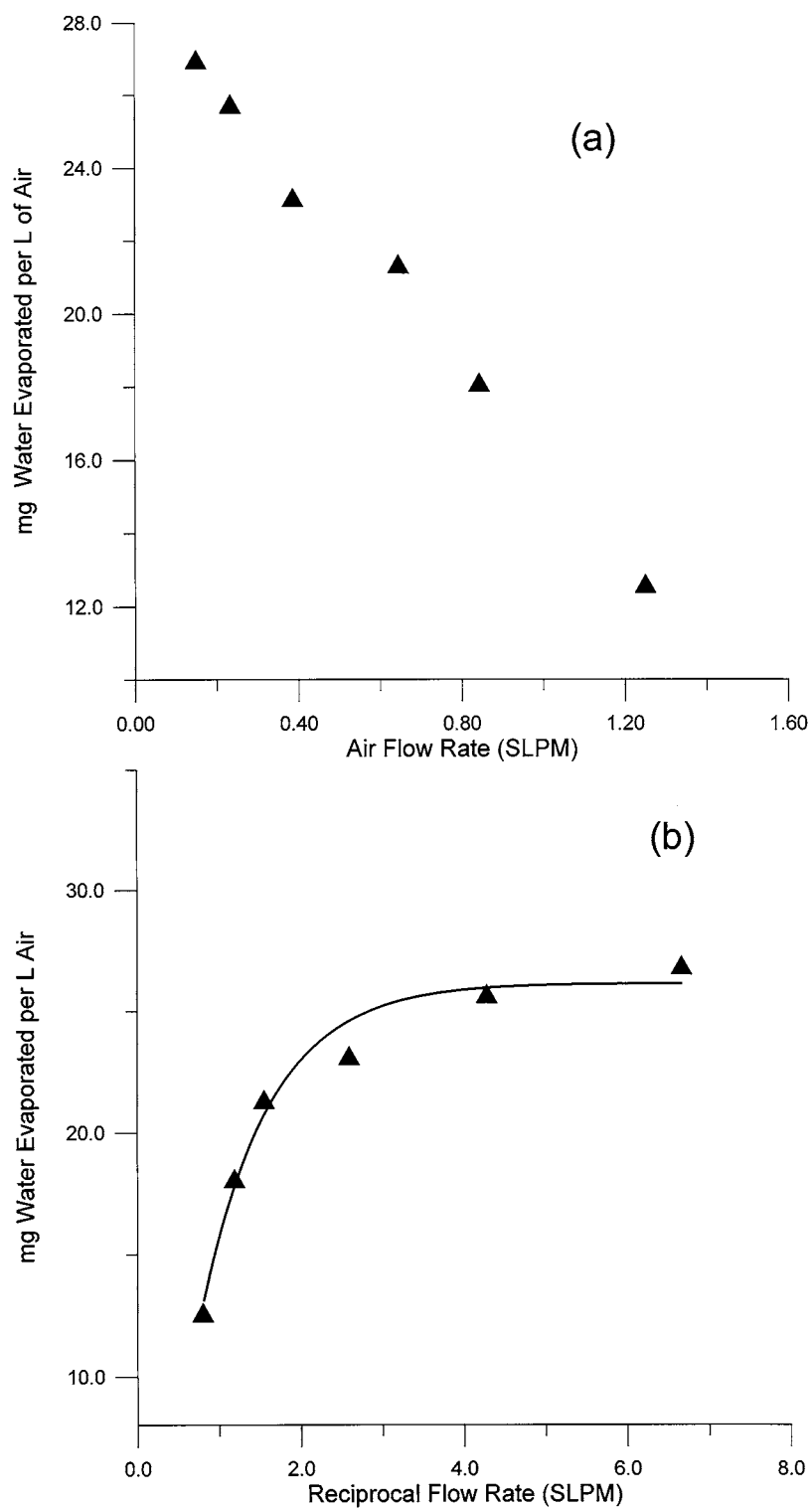


Fig. 3. (a) Evaporation loss per unit volume of air as a function of air flow rate; (b) evaporation loss per unit volume of air plotted as a function of the reciprocal air flow rate; the solid line represents the best fit line according to Eq. (1).



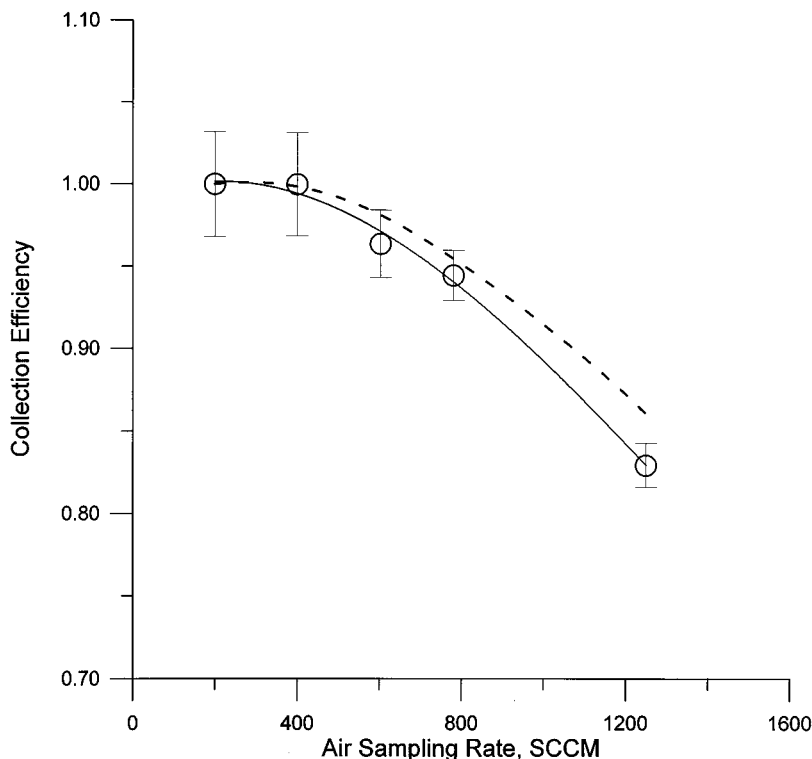


Fig. 4. Collection efficiency of the parallel plate diffusion denuder. The dashed line represents the computed theoretical efficiency and the solid line represents the best fit to the experimental data.

times. Lower air sampling rates will permit the use of small, battery powered air pumps that would greatly facilitate portability and field use.

Recently, we described a portable capillary ion chromatograph with suppressed conductometric detection for anion analysis [9]. The concentration Limits of detection (LODs) were comparable to standard bench-top IC systems but the mass LODs were better by  $>2$  orders of magnitude. The development of this capillary ion chromatograph led us to investigate the possibility of performing trace gas analysis with a miniaturized parallel plate denuder coupled to this system. Compared to previous work, the fabrication of the denuder is simpler and faster and an order of magnitude less sample flow rate is necessary to achieve parts per trillion level LODs. The design and performance of this instrument is reported in this paper.

## 2. Experimental

### 2.1. Thermally bonded silica coated wet effluent diffusion denuder

Two Plexiglas plates ( $22 \times 175 \times 3$  mm thick) were washed thoroughly with methanol followed by water and then allowed to dry. The plates were next covered with Teflon tape. The Teflon tape was then removed by a scalpel blade from the areas intended to constitute the wetted region. Silica particles (Aldrich), screened to give a size range of  $\sim 74$ – $127$   $\mu\text{m}$ , were used to coat the Plexiglas plates. An aluminum block was machined to internally contain a heating element; this assembly provided a hot surface for thermally bonding the silica particles to the Plexiglas plates. The filtered silica particles were placed on the aluminum block, heated to  $\sim 250^\circ\text{C}$ , for 10–15 min for preheating. One of the Plexiglas plates,



with the intended wettable area face down, was then placed on top of the heated silica particles and the aluminum block. A drill press, equipped with a flat aluminum plate, was used to press down the Plexiglas plate on the silica particles. Within a period of  $\sim 45$  s, the silica particles get imbedded into the semi-molten surface of the Plexiglas. This plate is removed and the procedure is repeated with the other plate. After cooling, the coated regions were rinsed with a high velocity water stream to remove the loosely held particles. The entire procedure was then repeated until the silica coating appeared to be uniform over the exposed area of the plates. Two to three repeats are generally sufficient. Thermal bonding of the silica particles to the Plexiglas according to the above procedure may result in slight deformation of the plates. Such deformations can be removed by placing the treated Plexiglas plate on top of a flat aluminum plate and placing in an oven at  $135^{\circ}\text{C}$  for 30 min.

The design of the parallel plate WEDD is shown in Fig. 1. The denuder was constructed using 3 mm thick Plexiglas plates. Fully assem-

bled, the shell of the PPDD measured  $2.2 \times 17.5 \times 0.75$  cm. The silica coated region SC was  $0.6 \times 10$  cm long. The silica coated region has a tapered V-shape at the bottom to facilitate liquid effluent collection. At the top and bottom of the silica coated region, holes were drilled to provide a liquid inlet LI and a liquid outlet LO. Stainless steel tubing (23 gauge) was push fit into these holes and epoxied in place. A 1.5 mm thick Plexiglas spacer PS, covered with Teflon film TF, was used to separate the two Plexiglas plates. The Teflon coated spacer completely covers the untreated edges of the plates and provides an inert surface for sampled gases entering the denuder. Spring-loaded clamps were placed all around the outer edges of the Plexiglas plates to seal the assembly. Air inlet tube AI and air outlet tube AO were made by thermally deforming Teflon tubing (4.6 mm i.d., 5 mm o.d.) to fit into the spacing between the Plexiglas plates. The air inlet/outlet tubes were roughened with sandpaper on the outside and epoxy adhesive was applied around it and on to the WEDD body to prevent any air leakage around these joints. The application of the adhesive also provides the desired rigidity to the inlet/outlet connections. Approximately 4 cm was left uncoated between the silica coating and the edge of the air inlet tubing to establish a laminar flow profile [1] before the sampled air comes into contact with the wetted area.

## 2.2. Gas phase calibration system

The gas phase portion of the analytical system was tested with different concentrations of  $\text{SO}_2$  as a test analyte. The basic arrangement has been described earlier [5]. Briefly, house air was cleaned and dried with a series of columns containing silica gel, activated charcoal, and soda lime. Sulfur dioxide standards were generated with a wafer type permeation device constructed in-house and maintained at  $30^{\circ}\text{C}$ . The device was gravimetrically calibrated and found to emit at a rate of  $24 \text{ ng SO}_2 \text{ min}^{-1}$ . Mass flow controllers (FC-280, Tylan General, San Diego, CA) were used to provide necessary dilution and flow control.

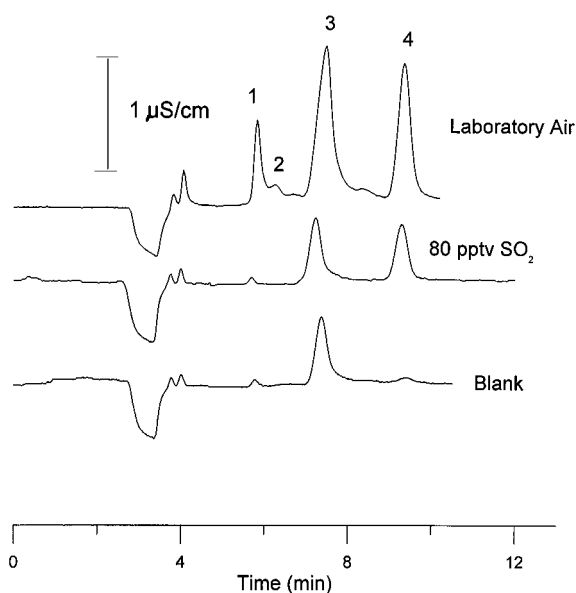


Fig. 5. Chromatogram resulting from sampling blank air and 80 pptv  $\text{SO}_2$  (both at 500 SCCM) and laboratory air (250 sccm). Peak identities: 1, chloride; 2, nitrite; 3, carbonate; 4, sulfate.



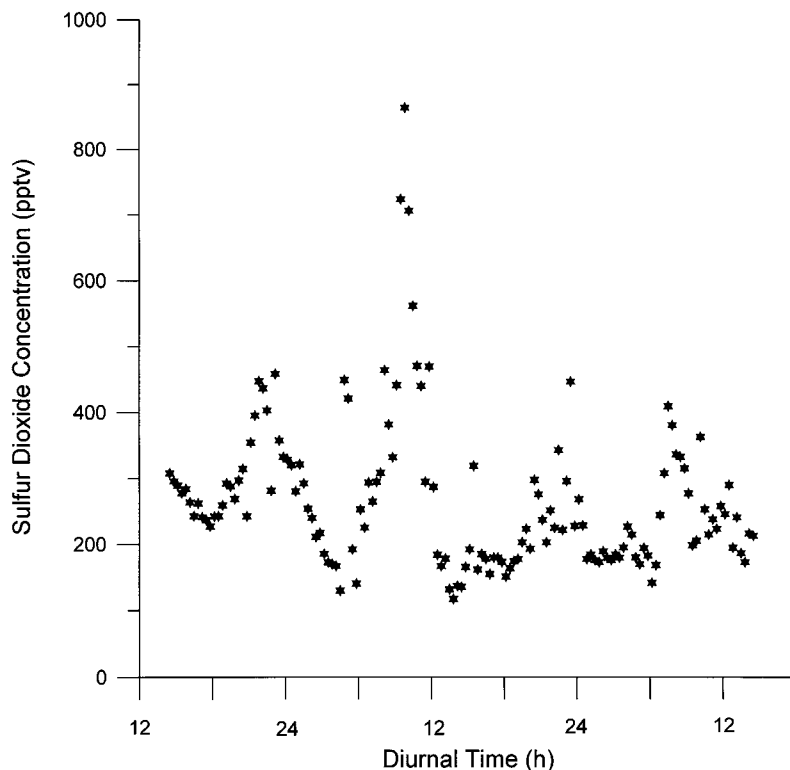


Fig. 6. Ambient air levels of SO<sub>2</sub> in Lubbock, TX over a 48 h period beginning Julian Day 119, 1998.

### 2.3. Liquid phase analytical system

The liquid phase portion of the instrument is shown in Fig. 2. Hydrogen peroxide (0.5 mM) is aspirated through a mixed bed deionizing column MB (Amberlite MB-1, Sigma, St. Louis, MO) to remove any ionic impurities present in the flow stream. The H<sub>2</sub>O<sub>2</sub> is then pumped to the liquid inlet ports of the WEDD using an eight-channel peristaltic pump PP (Minipuls 2, Gilson Medical Electronics, six channels are used in this work). The liquid effluent from the denuder is aspirated by two other channels of the same pump and sent to a degassing vial DV (holdup volume  $\leq 75$   $\mu$ l). The resulting liquid effluent, free from air bubbles, is pumped at a flow rate of 17  $\mu$ l min<sup>-1</sup> through a capillary preconcentration column PC (vide infra). A six port injection valve IV (Chem-inert model C3-1006EH, Valco, Houston, TX), shown schematically in Fig. 2, allows the preconcentrator column to be switched from the load to

the inject position and vice-versa. All data reported were obtained using a 10 min load/10 min inject cycle.

A previously described capillary scale suppressed conductometric IC [10] was used for separating, identifying and quantifying the sampled gas constituents. Briefly, this instrument consists of a syringe pump (Model 50300, Kloehe, Reno, NV) equipped with a 500  $\mu$ l glass syringe (Kloehe), a pressure sensor (Model SP-70-A3000, Senso-Metrics, Simi Valley, CA; provided with home-built electronics), the previously mentioned electrically actuated 6 port injection valve IV, an 180  $\mu$ m i.d., 35 cm long packed capillary analytical column (CC), a hollow fiber chemical suppressor [10], and a conductivity detector cell [9] connected to a Model ED40 electrochemical detector (Dionex, Sunnyvale, CA). Data acquisition was accomplished by an 80486 based PC via AI-450 software and an advanced computer interface, both from Dionex.



Capillary columns were packed in-house with AS-11 HC (high capacity) packing material from Dionex using a capillary version of the proprietary packing technique provided by Dionex. The preconcentration column consisted approximately of a 1.5 cm length of a 250  $\mu\text{m}$  i.d., 350  $\mu\text{m}$  o.d. packed capillary column. The exit frit for the precolumn was constructed as follows:  $\sim 1$  cm of the packing material was first removed from a 2.5 cm long packed capillary column. A small piece of a glass fiber filter (Whatman, type GF/A) was then inserted against the packing and held in place by a 50  $\mu\text{m}$  i.d., 150  $\mu\text{m}$  o.d. fused silica capillary that was pushed inside the larger bore capillary. The nested capillary assembly were then secured with epoxy adhesive into place. The preconcentrator column PC was connected to the injection valve in such a manner that the flow direction through PC remained the same in both the load and inject modes. Separations were performed using a 25 mM NaOH eluent hydroxide at a flow rate of 2.2  $\mu\text{l min}^{-1}$ . The retention time of sulfate was  $\sim 10$  min under these conditions. A 3.5 mM solution of sulfuric acid flowing at  $\leq 0.25$  ml  $\text{min}^{-1}$  functioned as suppressor regenerant and resulted in a suppressed conductance of  $\sim 1.8$   $\mu\text{S cm}^{-1}$ .

Sodium hydroxide eluents were prepared from a 50% NaOH stock solution (J.T. Baker). Hydrogen peroxide was prepared from a 30% stock solution (Mallinckrodt). Distilled deionized water with a specific resistivity of  $\geq 18$   $\text{M}\Omega \text{ cm}^{-1}$  was used to prepare all solutions. Analytical reagent grade chemicals were used throughout. Soda-lime traps were used to protect all solutions from  $\text{CO}_2$  intrusion.

#### 2.4. Determination of collection efficiency

The system was initially calibrated by preconcentrating different volumes (known flow rate passed through the preconcentrator column for different periods) of a 100  $\mu\text{g l}^{-1}$  sulfate standard. The collection efficiency for gaseous  $\text{SO}_2$  as a function of the air sampling rate was then determined by: (a) translating the observed response resulting from a given preconcentration period to an equivalent amount of sulfate with the help of

the above calibration; (b) accounting for the total denuder effluent liquid volume during that period (because of evaporation losses, the effluent liquid flow rate from the WEDD is less than the input liquid flow rate; the WEDD liquid output was therefore gravimetrically measured); and (c) comparing the number of moles of sulfate in the WEDD effluent from (a) and (b) above, to the number of moles of gaseous  $\text{SO}_2$  that was sampled through the system.

### 3. Results and discussion

#### 3.1. Thermally bonded WEDD

The ability to prepare an easily wettable surface is critical for fabricating WEDDs. Although several methods have been developed for chemically bonding silica particles to glass plates [3–5], we found that thermally bonding silica gel particles onto the surface of Plexiglas plates is a simple, viable option for preparing a highly wettable sampling surface. It does not require high temperature ovens, fragile glass components and caustic chemicals can be avoided. The procedure is conceptually similar to imbedding porous glass particles on the interior walls of a PTFE tube as described by Gnanasekaran and Mottola [11] by a thermal process and results in a easy to fabricate and robust device.

#### 3.2. Considerations on injection strategies

The success of any diffusion denuder based analysis approach depends on the ability of a denuder to collect the gaseous analyte of interest, preferably quantitatively. For a WEDD, it is further desirable to concentrate the analytes in the liquid effluent before separation and detection is performed. In a continuously operating WEDD, both the efficient uptake of the gaseous analyte by the denuder liquid and the subsequent concentration of the analytes in the effluent on a preconcentration column are important. The concentration of the analyte in the denuder effluent is maximized by minimizing the WEDD liquid flow rate. The input effluent flow rate down each plate of



the PPDD was  $15 \mu\text{l min}^{-1}$ . The effective thickness of the liquid film in the absence of air flow was determined by injecting a KCl solution at the top of the denuder and measuring its mean residence time with a miniature bifilar wire conductivity detector [12] placed immediately at the exit of the WEDD. From a knowledge of the liquid flow rate, and the total active area of the denuder, the maximum film thickness was computed to be  $\sim 70 \mu\text{m}$ . A small film thickness is critical to achieve a good concentration factor for the gaseous analyte while minimizing sample carry-over between successive determinations. Washout times with the present system were sufficiently small as to permit a new steady state signal to be fully established after one load/injection cycle following a step change in gas concentration at the denuder inlet.

A significant portion of the denuder input liquid evaporates during air sampling. The experimentally observed evaporation loss of water per liter ( $\mu\text{l l}^{-1}$ ) of sampled air as a function of air flow rate is shown in Fig. 3(a). Theoretically, a maximum loss of  $31 \mu\text{l l}^{-1}$  of sampled air (at  $30^\circ\text{C}$ ) would occur assuming the inlet air is completely dry and the air exiting the denuder is completely saturated with water. Experimentally, the evaporation loss was 87% of its maximum theoretical value ( $27 \mu\text{l l}^{-1}$ ) at an air flow rate of 0.150 standard liters per minute (SLPM), and dropped to 41% of the maximum theoretical limit ( $12.7 \mu\text{l l}^{-1}$ ) at an air flow rate of 1.250 SLPM. At high air flow rates, the equilibration of the air flowing through the denuder with the liquid surface becomes the primary factor governing evaporation. The expression for determining the theoretical amount of water evaporated at a specific air flow rate is the same type of equation used for determining the collection efficiency of denuders [3]:

$$1 - aW = be^{-c/Q} \quad (1)$$

where  $a$ ,  $b$ , and  $c$  are constants,  $Q$  is the volumetric flow rate, and  $W$  is the amount of water evaporated per liter of air. Fig. 3(b) shows  $W$  plotted against the reciprocal air flow rate with the solid line representing the best fit to Eq. (1) ( $a = 0.0381$ ,  $b = 1.305$ ,  $c = 1.182$ ). Under the max-

imum air flow rate tested with this denuder (1.25 SLPM), no dry spots developed over the active sampling surface of the PPDD using a liquid flow rate of  $15 \mu\text{l min}^{-1}$  down each plate.

The liquid aspiration rate and the liquid influent flow rates in to the WEDD were maintained the same,  $15 \mu\text{l min}^{-1}$  per plate. Due to the evaporation losses during air sampling, the aspiration rate is greater than the actual effluent flow rate at the bottom of the denuder. This causes air bubbles to be present in the effluent stream. The operating pressure of the capillary ion chromatograph was  $\sim 500$  psi at a flow rate of  $2.2 \mu\text{l min}^{-1}$ . This pressure was not sufficient to dissolve air bubbles present in the WEDD effluent. Under the circumstances, there are two alternatives to inject a bubble-free sample into the IC. The first alternative is to pump the entire denuder effluent through the precolumn followed by washing with degassed deionized water for a period of time to remove any bubbles trapped on the precolumn. The second alternative is the use of a degassing vial between the denuder exit and the precolumn. The degassing vial acts as a gravity based air separator-bubble free liquid aspirated from the bottom can be loaded onto the preconcentrator column. In the present work, the degassing vial alternative was chosen. Also, the six-port injector used in the present work permitted the use of only one preconcentrator column. Therefore the system was so configured as to apply aspiration to the degassing vial at a greater flow rate when the valve is in the inject position to empty it rapidly and minimize sample carryover. Eight port injector valves are commercially available that would allow the loading of one preconcentrator column while the other one is washed/chromatographed. Such an arrangement will benefit more from the first degassing alternative.

### 3.3. Preconcentration column

In a previous paper [9], the preconcentration of analytes using a 10 cm long packed capillary preconcentrator column was demonstrated. While analyte preconcentration using such a column was feasible in the present application, several im-



provements were desired. Firstly, the preconcentration column was sufficiently long so that the maximum flow rates through this column achievable by a peristaltic pump were much smaller than desired. Secondly, a carbonate peak that is always present in air samples and peaks from other impurities present in the  $\text{H}_2\text{O}_2$  solution put through the WEDD interfered with the determination of low level analyte peaks. The presently developed preconcentrator column provided solutions to these two problems. A 1.5 cm long packed capillary column with a cross sectional area ( $250\text{ }\mu\text{m}$  i.d.) nearly twice as large as that of the separation column ( $180\text{ }\mu\text{m}$  i.d.) provided sufficient capacity for typical ambient air applications. This pre-column permitted flow rates up to  $18\text{ }\mu\text{L min}^{-1}$  with a peristaltic pump relative to  $\sim 3\text{ }\mu\text{L min}^{-1}$  obtained with the precolumn used. In addition, passing the aqueous  $\text{H}_2\text{O}_2$  through a mixed bed ion exchanger before the WEDD was found to remove ionic impurities that interfered with the chromatographic determination of the analytes. In the absence of  $\text{H}_2\text{O}_2$  in the WEDD liquid,  $\text{SO}_2$  is oxidized partially to sulfate resulting in both sulfite and sulfate peaks from sampling  $\text{SO}_2$ . Using dilute  $\text{H}_2\text{O}_2$  results only in sulfate which improves and simplifies quantitation. There is no significant oxidation of collected nitrite to nitrate by  $\text{H}_2\text{O}_2$ .

### 3.4. Collection efficiency

The collection efficiency  $f$  for a parallel plate diffusion denuder is given by [5,13]

$$f = 1 - 0.91e^{-3.77\alpha DL/Q} \quad (2)$$

where  $D$  is the diffusion coefficient of the gas ( $0.13\text{ cm}^2\text{ s}^{-1}$  for  $\text{SO}_2$  [14]),  $L$  is the length of the tube, and  $Q$  is the volumetric flow rate. For a parallel plate denuder, the parameter  $\alpha$  is given by:

$$\alpha = 2b/a \quad (3)$$

where  $a$  and  $b$  are the short and long dimensions of the active cross section of the denuder, respectively [13].

The collection efficiency for the parallel plate WEDD is shown graphically in Fig. 4 for low to

sub-ppbv levels of  $\text{SO}_2$ . The solid line shows the collection efficiency for the WEDD whereas the dashed line shows the theoretical collection efficiency. Error bars represent  $\pm 1\text{ SD}$  ( $n = 3$ ). Collection efficiency is essentially unity up to  $\sim 500\text{ cm}^3\text{ min}^{-1}$  (SCCM) air sampling rate and drops to  $\sim 83\%$  collection efficiency at 1250 SCCM. The theoretical collection efficiency for the WEDD at 1250 SCCM is  $\sim 85\%$ . This difference is well within the uncertainty of the diffusion coefficient value of  $\text{SO}_2$  used for the calculations. In terms of diffusion coefficients for various gases, the diffusion coefficient for  $\text{SO}_2$  is on the low end among those of common inorganic gases of interest and other soluble ionogenic gases such as HONO, HCl,  $\text{HNO}_3$ , etc. would be expected to be collected at least as efficiently as  $\text{SO}_2$ .

### 3.5. Response linearity and detection limits

An air sampling rate of 500 SCCM was chosen to evaluate the WEDD such that the collection efficiency is still essentially quantitative. The response linearity was studied over a  $\text{SO}_2$  concentration range 20–2000 pptv. Higher concentrations of  $\text{SO}_2$  result in nonlinear responses in the present detection system unless the sampling period or the sampling rate is reduced. However, the ambient  $\text{SO}_2$  levels at our location are low and this range is adequate for ambient measurements, without reducing the sampling period. The linear  $r^2$  value of the sulfate peak height vs. the sampled  $\text{SO}_2$  concentration was 0.9980 for the entire concentration range. The relative standard deviation (RSD) was  $\leq 3.2\%$  over this concentration range for each concentration sampled. Based on the uncertainty of the blank and the slope of the calibration plot, the limit of detection was determined to be 1.6 pptv ( $S/N = 3$ ). Fig. 5 shows a chromatogram resulting from the sampling of clean air and  $\sim 80\text{ pptv}$   $\text{SO}_2$ .

### 3.6. Ambient air studies

Laboratory air and ambient Lubbock air were sampled to evaluate system performance. A chromatogram resulting from sampling laboratory air is shown in Fig. 5. The system was operated at an



air sampling rate of 250 SCCM, to deliberately limit the response. The SO<sub>2</sub> concentration in this sample was determined to be ~400 pptv; this demonstrates the excellent SO<sub>2</sub> response even at low air sampling rates. In addition the sample also shows the presence of ~30 pptv HCl and ~2 pptv HONO.

Sulfur dioxide concentrations in Lubbock, TX were studied over a 48 h period where the WEDD was allowed to operate continuously for this time period without any user intervention. The results are shown in Fig. 6. These results correlate well with previously measured ambient SO<sub>2</sub> levels at this location [3].

In conclusion, a compact, inexpensive air sampling system has been developed capable of measuring down to low parts per trillion levels of SO<sub>2</sub> and similar other gases. The entire instrument can easily be transported into the field for analysis. Not only can this system be adapted for the simultaneous analysis of a number of gases, it can be easily automated and operate continuously for prolonged periods without any user intervention.

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